# HALIDE EUTECTIC GROWTH

By

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## SUMMARY

Fiberlike NaCl-NaF eutectic mixtures have been produced on earth and in space by the directional solidification technique. It was found that continuous and discontinuous NaF fibers were embedded in a NaCl matrix from ingots grown in space and on earth, respectively. The production of continuous fibers in a eutectic mixture was attributed to the absence of convection current in the liquid during solidification.

Macroscopic and microscopic examinations on longitudinal and transverse sections of space-grown and earth-grown ingots were made. It was found that during the major portion of the space solidification process, the NaF fibers were aligned with the ingot axis. However, they were normal to it during the very beginning of the solidification process. This indicated that the direction of heat flow was perpendicular to the ingot axis. The best microstructures were obtained from ingots grown in space. These microstructures were compared with those produced on earth with and without convection current in the liquid during growth.

Optical transmittance measurements of transverse and longitudinal sections of the space-grown and earth-grown ingots were carried out with a polarizer in a Perkin Elmer Spectrometer. It was found that for a given sample thickness, the highest percentage of transmittance was obtained from ingots grown in space. The effect of sample thickness on transmittance was investigated. It was found that the thinner the sample, the higher the transmittance over a range of wavelengths, in agreement with the general optical property of transparent materials exposed to electromagnetic waves.

## INTRODUCTION

When certain binary eutectic mixtures solidify, one of the two phases can form fibers or platelets in a matrix of the second phase. For example, when a eutectic liquid of NaCl and NaF solidifies, fibers of NaF form in a matrix of NaCl.

Fiberlike and platelike eutectics produced on earth are limited in perfection by the presence of a banded structure,[1,2] discontinuity, [3] and faults [4,5] due, at least in part, to vibration and convection currents in the melt during solidification. The presence of these defects renders the solid-state eutectic devices inefficient and useless [6].

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If the solidification process is performed in a space environment, where there is no vibration and convection current in the melt, there is reason to believe that continuous fiberlike eutectic microstructures can be produced. The electric, thermomagnetic, optical, and superconducting characteristics of such fibers will be strongly anisotropic, and this will make possible various exciting device applications.

The purposes of this paper are (1) to prepare, in a space experiment, fiberlike NaCl-NaF eutectic with continuous NaF fibers embedded in a NaCl matrix and to examine the eutectic microstructure, and (2) to measure the relevant optical properties of the space-grown and earth-grown eutectics. Explanations of the differences in properties are given in terms of the scattering and absorption characteristic of the materials.

## EXPERIMENTAL PROCEDURE

Experimental studies have been carried out at UCLA to acquire all possible knowledge of the solidification process of the eutectic mixture involved, short of doing the space experiments themselves. Calculations and design of equipment have been followed by a program of solidifications at various rates and with various temperature gradients at the interface.

The objective of the earth-based studies is to maximize the likelihood of success of the space experiments.

Ingots of NaCl-NaF eutectics, 0.31 inch in diameter and 2.5 inches long have been grown unidirectionally on earth and in the Skylab in a multipurpose furnace at one freezing rate and a steep temperature gradient.

## RESULTS AND DISCUSSION

The experimental results are divided into three parts: The first part concerns the macroscopic and microscopic examinations of the samples that were grown in Skylab 3 and samples that were grown on earth. The second part concerns the preparation of continuous NaF fibers embedded in a NaCl matrix. The third part concerns the optical property of the NaCl-NaF eutectic. Comparison of the experimental results between the earth-grown and space-grown samples will be discussed in terms of scattering and absorption characteristic of the eutectic.

### A. Macroscopic and Microscopic Examinations of Microstructures

Figure 1 is a macro-photograph showing the appearance of the three ampoules after the Skylab experiments. The surfaces of the stainless steel cylinders and the copper tubings (right side of Fig. 1) were in perfect condition, indicating that there was no reaction between the ampoules and the cartridges. Remelting of the silver solder was not detected at the joint binding the stainless steel cylinder and the copper tubing together.

Figure 2 is a macro-photograph of the three samples taken out of the ampoules by grinding off the welded ends of each cylinder. Careful inspection on the surface of the sample revealed no reaction between the the NaCl-NaF eutectic and graphite container. In sample M564-10, two transverse fractured surfaces of the ingot occurred, both close to the head and tail portions of the sample as revealed in Fig. 2. However, the fracture did not interrupt the growth pattern of the ingot.

Figure 3 is a macro-photograph showing the solid-liquid interface, columnar grains of the solidified portion of the sample (on the right of the interface), and the unsolidified portion of the sample (on the left of the interface). An enlarged portion of the solid-liquid interface is given in Fig. 4 which shows that at the beginning of the solidification process, the NaF fibers were grown in the direction perpendicular to the growth direction. This indicates that the direction of heat extraction during the onset of solidification is normal to the growth direction in contrast to what was originally designed. This was tentatively attributed to improper insulation design. However, in a distance not far away from the initial solid-liquid interface (about 0.12 cm), the NaF fibers began to align toward the growth direction.

A representative photomicrograph of perfect and continuous fibers is given in Fig. 5 which shows that the NaF fibers are regularly spaced and parallel to the growth axis. When the NaCl-NaF eutectic was grown on earth with convection currents, the resulting eutectic microstructure is represented by Fig. 6 which shows that the solidified NaF fibers are randomly embedded in the NaCl matrix along the longitudinal section of the ingot. When the same eutectic was solidified vertically with very little convection current in the liquid during growth, the NaF fibers as revealed by Fig. 7 are regularly distributed along the ingot axis. However, these fibers are partially discontinuous.

A photomicrograph of the transverse section of the Skylab-grown sample is shown in Fig. 8 which reveals the shapes of the fibers which are preferentially rectangular. A scanning electron photomicrograph of the shapes of fibers is given in Fig. 9 which is the perspective view of the rectangular NaF fibers, sticking out of the continuous NaCl matrix.

Single-grain eutectic has not been produced in the presence of micro-gravity in space as evidenced in Fig. 10 which is a transverse section of sample M564-10. Many grains and subgrains are present throughout the whole cross-section. However, the fibers are aligned very regularly and parallel to the growth direction. Evidence in supporting the above statement is given in Fig. 11a which is a picture taken from Sample M564-6 which was grown in space. A filtered light from a Bausch & Lomb microscope was shone at the tail end of the sample. Due to good alignment of NaF fibers along the sample axis, light was transmitted from the tail end to the melted solid-liquid interface which is about 1.4 cm away from the "head" of the sample. Light was not transmitted through the unmelted portion of the sample because that portion of the ingot was grown on earth and the fibers did not line up with the sample axis. Note the homogeneity of the sample as revealed in Fig. 11a. Fig. 11b is a portion of a NaCl-NaF eutectic sample grown vertically on earth in a prototype furnace with very little convection current in the melt during growth. Light was completely transmitted from one end to the other, indicating that the NaF fibers are aligned in the direction of the growth axis. However, many striations appeared on the surface of the cylindrical sample, indicating the presence of non-homogeneity in the sample. In the absence of gravity (or in a microgravity environment), a non-homogeneous crystal can be transformed to a homogeneous one if it is grown in a space environment. Fig. 11c is a picture taken from a sample grown in an induction furnace at UCLA. An attempt was made to shine a light at one end of the sample but it did not travel very far because the NaF fibers were not aligned in the direction of the light. However, when light was shone on the side of the sample as indicated by the white spot in Fig. 11c, transmittance of light occurred in the direction perpendicular to the sample axis, indicating that the fibers are also perpendicular to the sample axis. Banded microstructure was evidenced in Fig. 11c in agreement with our original prediction.

## B. Sodium Flouride Fibers

In a zero-gravity environment, there is no convection current in the liquid during solidification and there is no difficulty in mixing two liquid phases of different densities. Furthermore, vibration levels in space will be far lower than those on earth. Consequently, a continuous fiber eutectic mixture can be produced in a space environment, and microstructure sensitive to convection currents and vibration can develop undisturbed.

Fig. 12a is a macrophotograph of a space-grown ingot (M564-11) which has been immersed in methane alcohol for five weeks. The surface of the undissolved portion of the ingot is encased with a skeleton of NaF fibers. An enlarged portion of the ingot containing the unsolidified portion, the curved solid-liquid interface and the solidified portion is given in Fig. 12b. Notice that on the right-hand side of the interface, the undissolved portion of the eutectic ingot reveals the presence of directional grains along the ingot axis. However, the grain directionality was not evident in the unsolidified portion of the ingot, indicating that the fibers are short and randomly distributed. Figure 13a proves that the growth of fibers was originated at the solid-liquid interface. Figure 13b is a picture of the end cross-section of the unsolidified portion of the ingot, showing that the short NaF fibers are perpendicular to the cylindrical surface of the ingot.

## C. Optical Property

Image transmission properties similar to those of fiber optic materials were obtained with an NaCl-NaF eutectic [7]. Moreover, this eutectic was found to be far-field infrared transmitting medium for wavelengths longer than the inter-fiber distance. Since the NaCl-NaF eutectic used for optical measurement has discontinuous NaF fibers embedded in the NaCl matrix, far better results will be obtained if the same eutectic can be produced in space with continuous fibers.

Figure 14 is a plot of transmittance versus wave number, k ($40 \times 10^2 cm^{-1}$ to $4 \times 10^2 cm^{-1}$) for NaCl, NaF and NaCl-NaF eutectics, prepared at UCLA, reported previously, and grown in the Skylab. The eutectic sample thicknesses taken from the transverse sections of the ingots were 0.107 in. The transmittance of NaCl drops off abruptly at $k = 7 \times 10^2 cm^{-1}$ and that of NaF at $k = 10 \times 10^2 cm^{-1}$ because the former has a higher refractive index (1.54) than the latter (1.31). Due to the optiaal mode of lattice vibration, the transmittance of NaCl and NaF approach zero at $k = 4.5 \times 10^2 cm^{-1}$ and $6.8 \times 10^2 cm^{-1}$, respectively. For the NaCl-NaF eutectic grown at UCLA where there were convection currents present in the liquid during growth, the transmittance was about 10% over a narrow range of wave numbers as indicated in Fig. 14. When the same eutectic was grown in space (M564-6) where there were no convection currents in the liquid during growth, the transmittance was increased to 65% over a much larger range of wave numbers. This was attributed to the achievement of producing continuous NaF fibers embedded in a continuous NaCl matrix so that the losses due to reflection and refraction of light within the eutectic specimen have been greatly reduced. The shape of the transmission curve for the NaCl-NaF eutectic is of great interest. At $k > 30 \times 10^2 cm^{-1}$, the transmittances of the two eutectics approach zero while those of NaCl and NaF remain at 95%. The explanation is that the interfacial atoms at the fiber-matrix interface are mismatched. When incident light is directed at the surface of a eutectic sample, a fraction of the incident light transmitted through the eutectic sample will decrease due to scattering. This observation is in agreement with the fact that the higher the wavenumber (or the shorter the wavelength) the higher the scattering. The scattering effect of the space-grown sample is not as severe as that of the earth-grown sample (B.D.G.) because the NaF fibers in the former are continuous while those in the latter are discontinuous. The decrease in transmittance for wave numbers less than $8.0 \times 10^2 cm^{-1}$ was attributed to absorption by the NaF fibers.

The effect of thickness on the transmission curve is given in Fig. 15 which indicates that the thinner the sample, the higher is the transmittance for a fixed wave number. This observation is in agreement with Lambert's law of absorption. The basic principle from which the law was derived is that the fraction of radiation absorbed in passing through a thin layer of matter is proportional to the thickness of the layer and the absorption coefficient which depends upon the nature of the absorbing matter and the wave length of the radiation. Expressed mathematically, where $I_o$ is the intensity of incident radiation upon a thin layer of matter and I is the intensity of the radiation that passes through the matter, one obtains

$$\frac{I_o - I}{I_o} = \frac{\Delta I}{I_o} = -\mu_\ell \Delta X \tag{1}$$

where $\Delta X$ is the thickness of the matter and $\mu_\ell$ is the linear absorption coefficient for the particular material and wavelength concerned. The negative sign arises because $\Delta I$ is a mathematical symbol for the increase in intensity I of the radiation as it passes through the layer of matter.

The effect of surface condition on the transmission curve for both the transverse and longitudinal sections of the NaCl-NaF eutectic, grown vertically on earth is given in Figs. 16 and 17 respectively. The data indicated the intensity of the transmitted light decreased with etching over the whole range of wave number. This can be explained by the fact that etching resulted in the roughening of the sample surfaces. When a light is shone on a rough surface, the intensity of the transmitted light decreases as the degree of roughness increases, in agreement with experimental observations. However, there was an absorption band at $k \simeq 10 \times 10^2 cm^{-1}$ for both cases after etching. This was tentatively attributed to the presence of impurities in these specimens.

## CONCLUSIONS

The following conclusions can be drawn from this investigation:
1. Continuous NaF fibers have been produced in the Skylab experiments. The success in producing continuous fibers is due to the absence of convection current in the liquid during solidification.
2. Larger transmittance over a wider wavelength was obtained from the Skylab-grown ingots. This is due to excellent alignment of NaF fibers embedded in the NaCl matrix.

## ACKNOWLEDGMENT

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## REFERENCES

1. A.S. Yue and J.B. Clark: Trans. TMS-AIME, 1961.
2. F.D. Lemkey and E.R. Thompson: Met. Trans., 1971, Vol. 2, p. 1537.
3. F.W. Crossman and A.S. Yue: Met. Trans., 1971, Vol. e, p. 1545.
4. A.S. Yue: Trans. TMS-AIME, 1962, Vol. 224, p. 1010.
5. R.W. Kraff and D.L. Albright: Trans. TMS-AIME, 1961, Vol. 221, p. 95.
6. H. Weiss: Met. Trans., 1971, Vol. 2, p. 1513.
7. J.A. Batt, F.C. Douglas, F.S. Galasso, Ceramic Bulletin, 1969, Vol. 48, No. 6, p. 622.

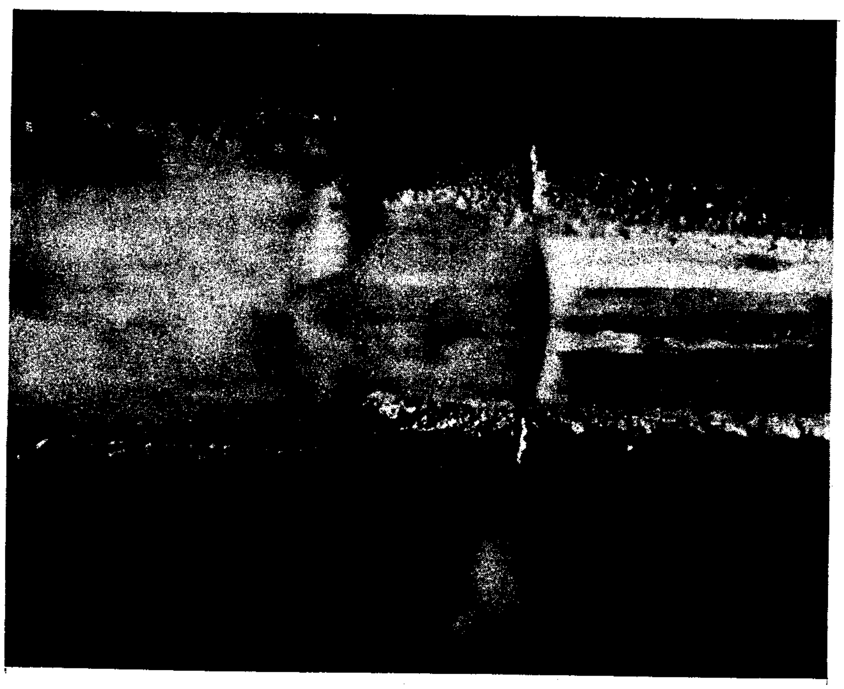


FIGURE 3. MACROGRAPH SHOWING THE SOLID-LIQUID INTERFACE OF THE SKYLAB GROWN NaCl-NaF EUTECTIC (6.5X)

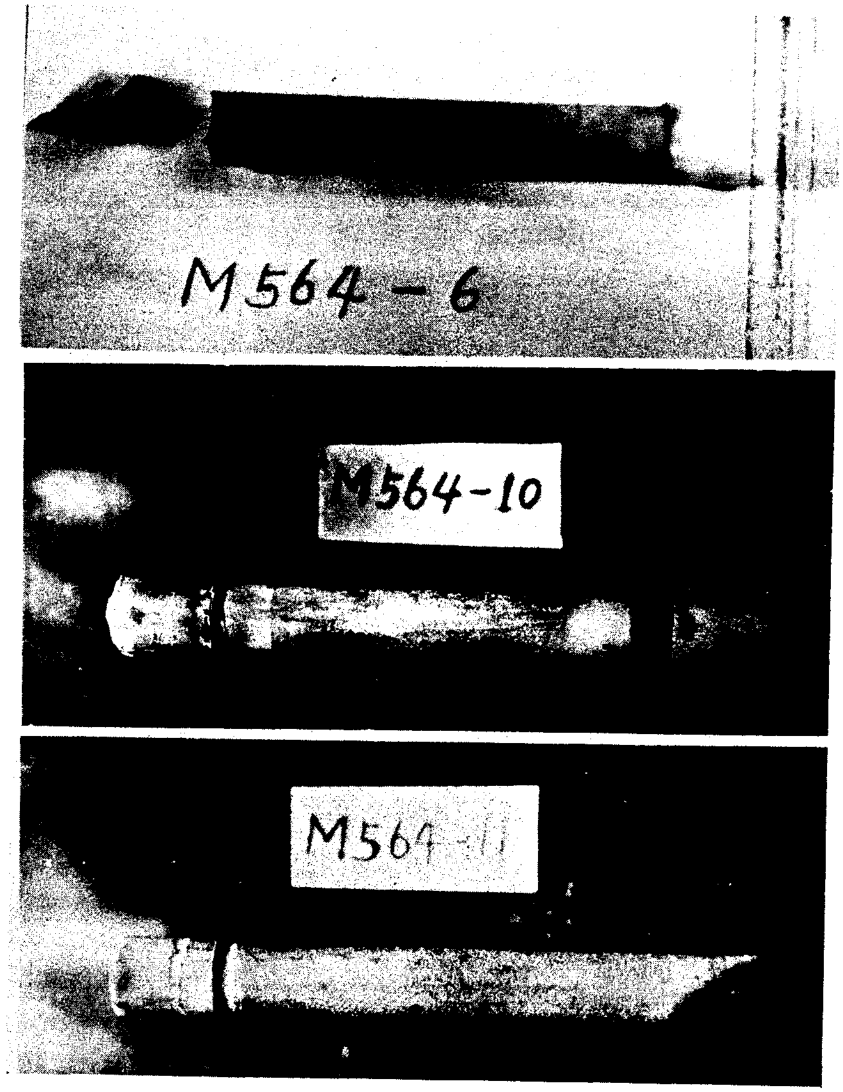



FIGURE 2. MACRO-PHOTOGRAPH OF THE NaCl-NaF EUTECTIC GROWN IN THE SKYLAB

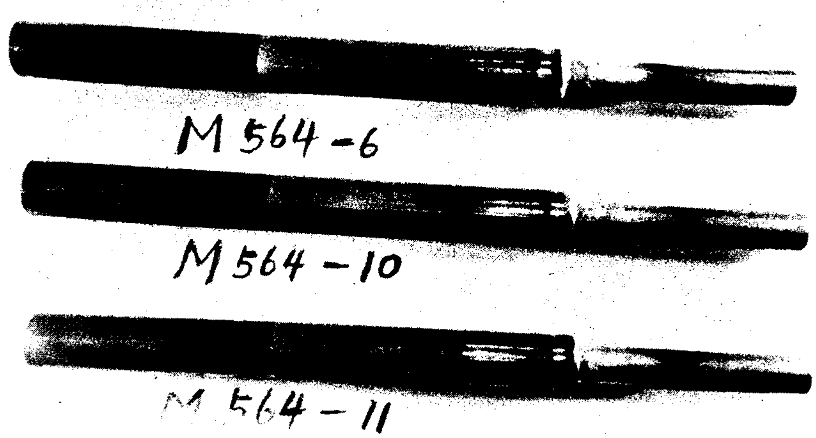



**FIGURE 1. PHOTOMACROGRAPH OF THREE AMPOULES (0.8X)**

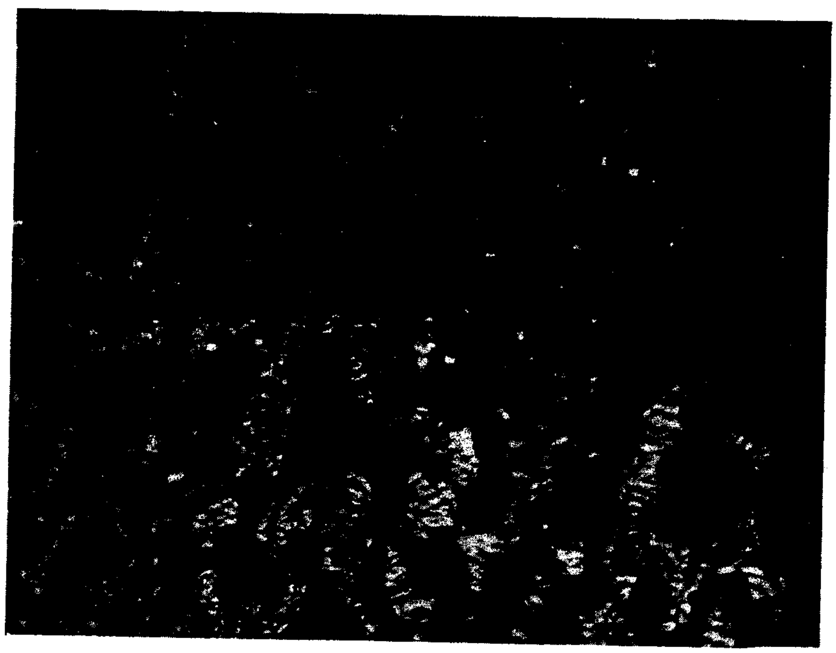


FIGURE 4. ENLARGED PORTION OF THE SOLID-LIQUID INTERFACE (410X)

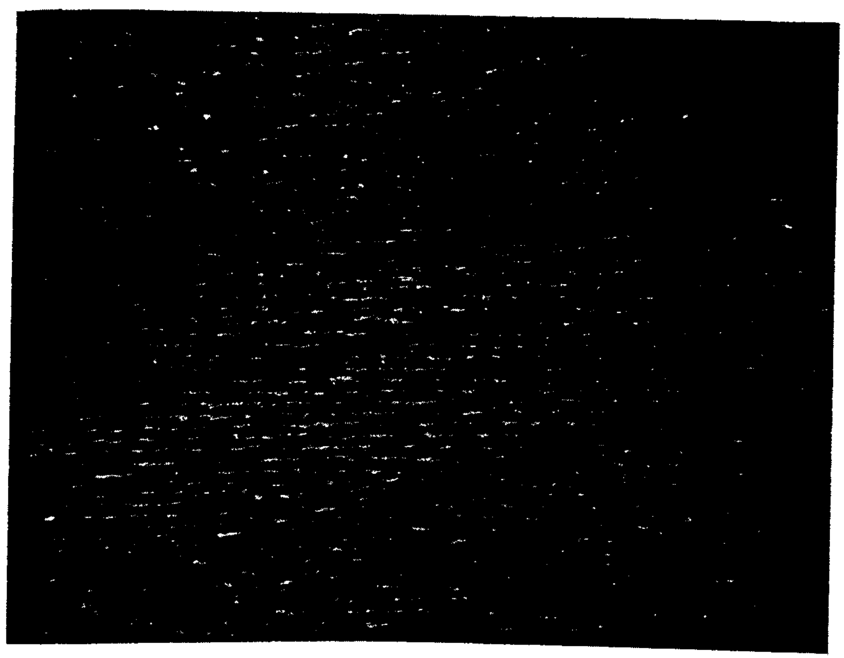


FIGURE 5. PHOTOMICROGRAPHS OF THE LONGITUDINAL SECTION OF THE NaCl-NaF EUTECTIC SHOWING CONTINUOUS NaF FIBERS (135X)

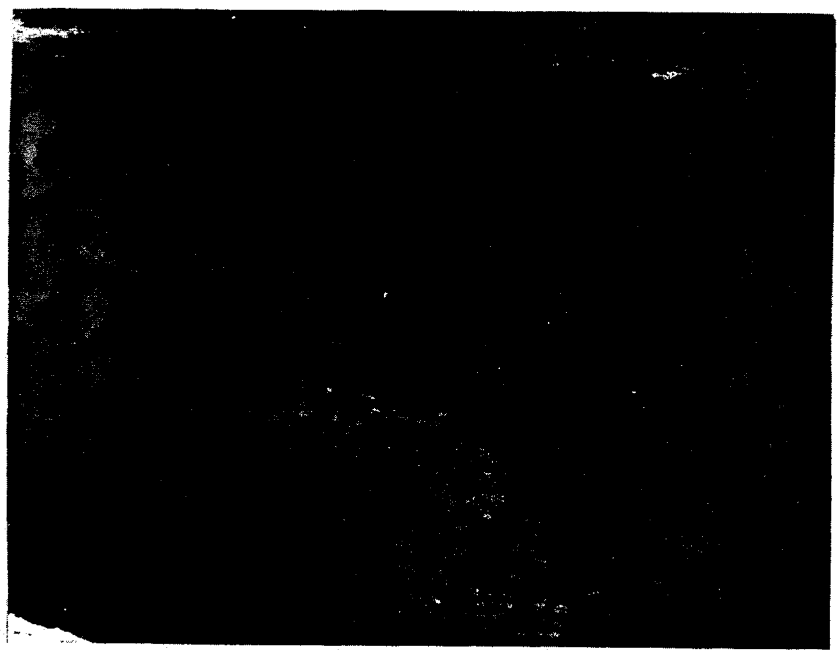


FIGURE 6. PHOTOMICROGRAPHS OF THE LONGITUDINAL SECTION OF NaCl-NaF EUTECTIC SHOWING DISCONTINUOUS NaF FIBERS (1500X)

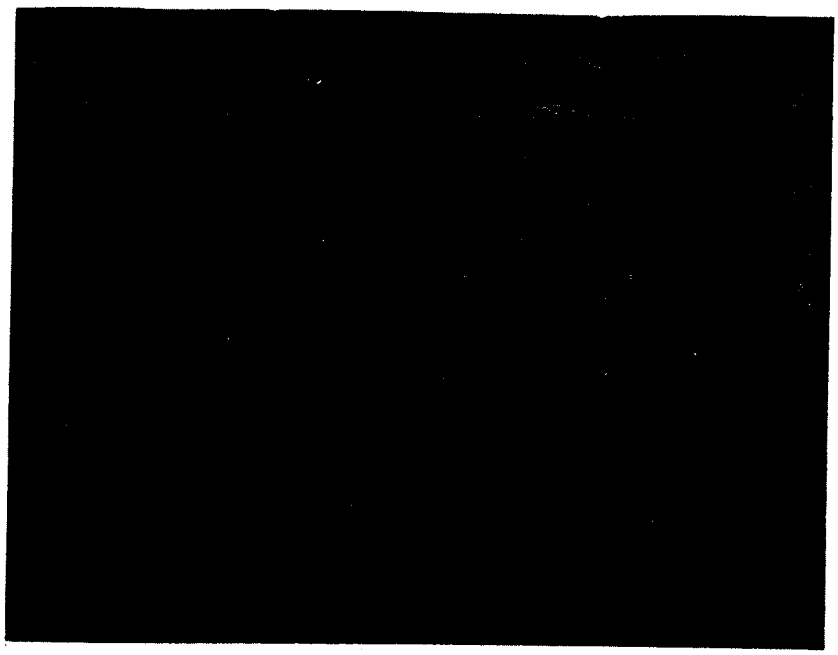


FIGURE 7. PHOTOMICROGRAPH OF LONGITUDINAL SECTION OF NaCl–NaF EUTECTIC SHOWING SOME DISCONTINUOUS NaF FIBERS (1500X)

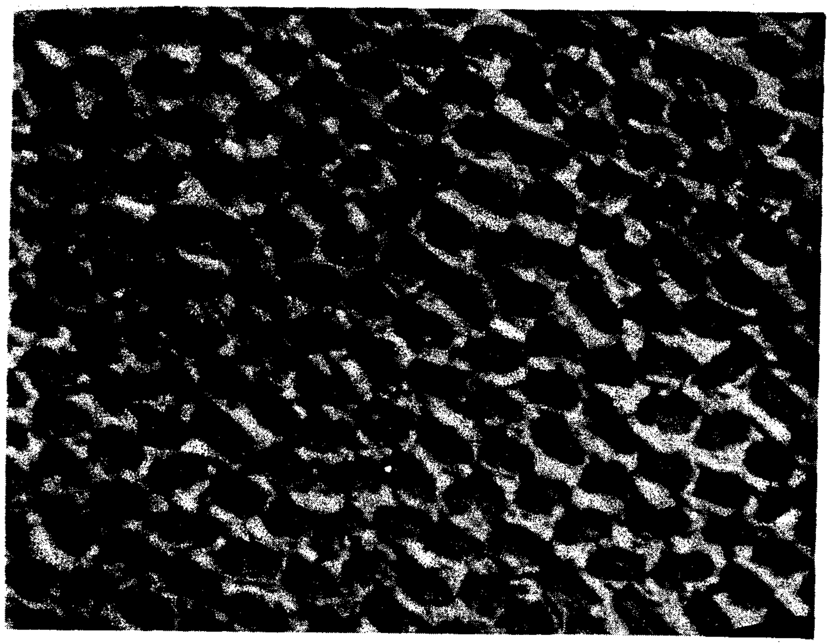


FIGURE 8. PHOTOMICROGRAPH OF THE TRANSVERSE SECTION SHOWING SHAPES OF NaF FIBERS (1500X)

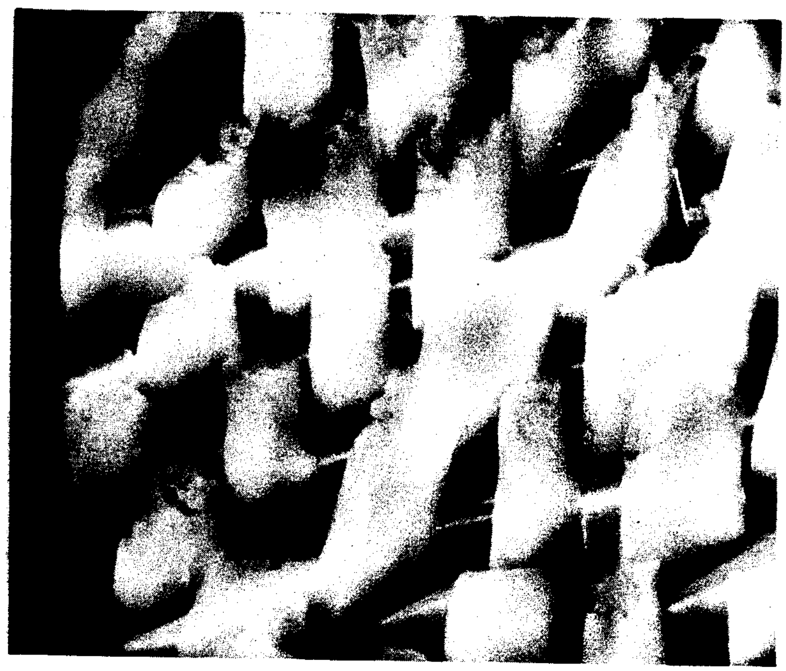
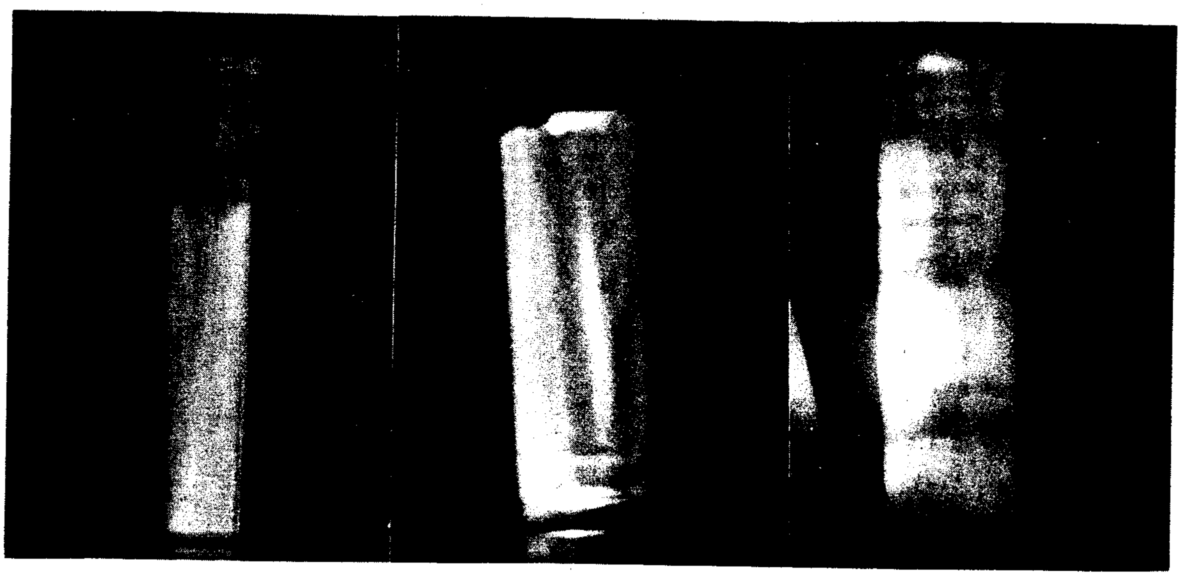


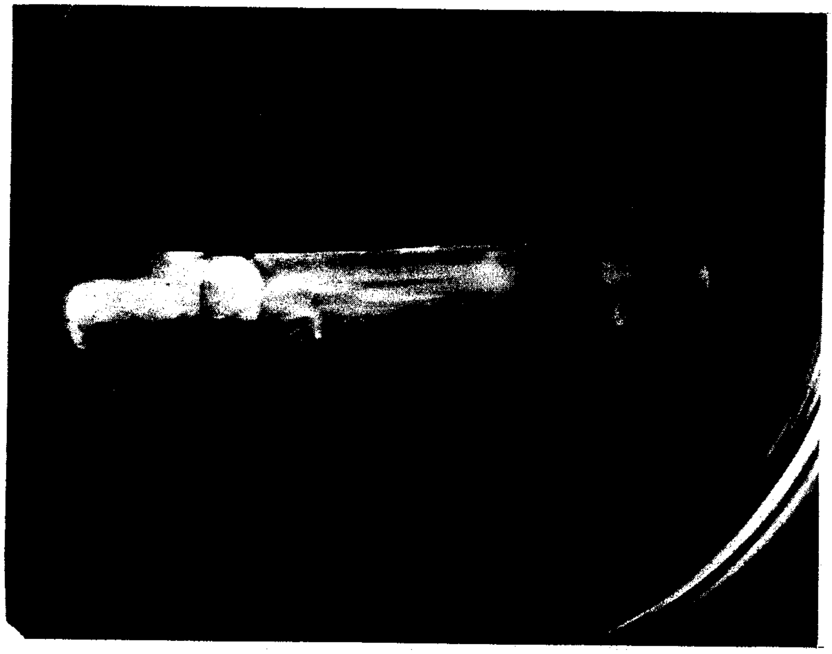
FIGURE 9. SCANNING ELECTRON PHOTOMICROGRAPH SHOWING THE NaF FIBERS (2100X)

FIGURE 10. MACROPHOTOGRAPH OF THE TRANSVERSE SECTION OF THE NaCl-NaF EUTECTIC, SHOWING GRAINS AND SUBGRAINS (9X)

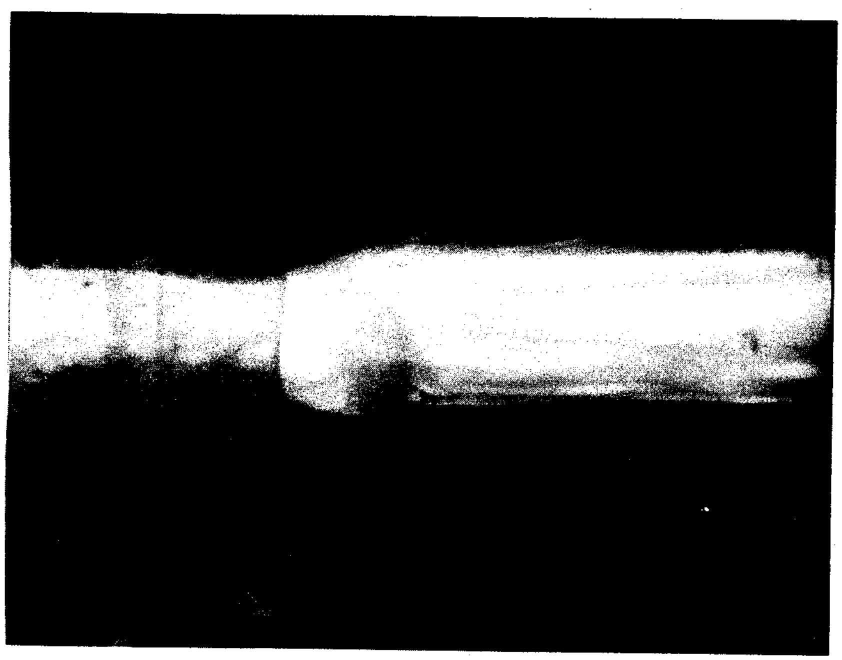


(a) (b) (c)

FIGURE 11. MACROPHOTOGRAPHS OF SKYLAB-GROWN (a), NASA-GROWN (b), AND EARTH-GROWN (c) NaCl-NaF EUTECTIC



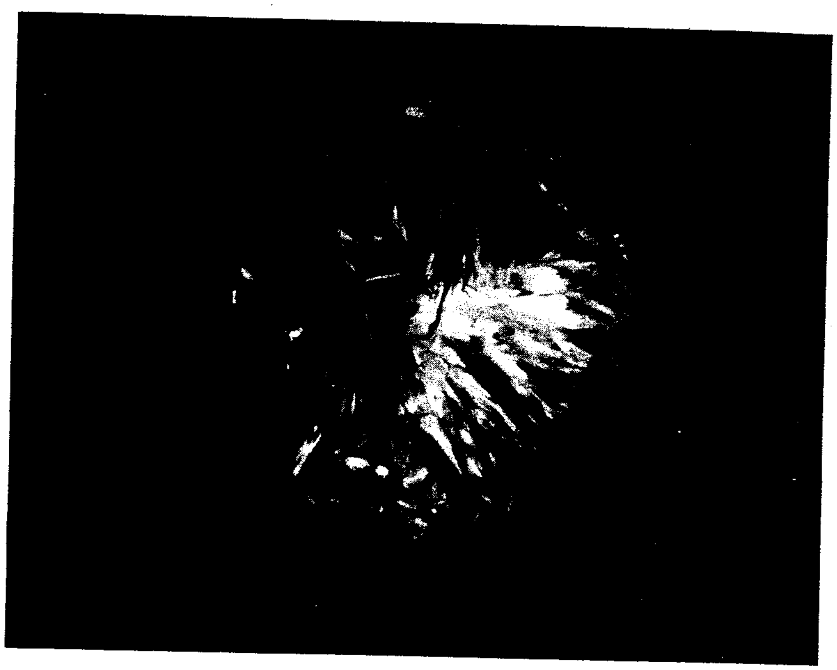
12a



12b

FIGURE 12. SKYLAB GROWN INGOTS (M564-11) ENCASED WITH NaF FIBERS ETCHED OUT FROM NaCl-NaF EUTECTIC. (a) 2X AND (b) 4.3X

13a



13b

FIGURE 13. (a) NaF FIBERS GROWN FROM THE SOLID-LIQUID INTERFACE.
(b) DISCONTINUOUS AND RANDOMLY ORIENTED FIBERS OF THE END INGOT.

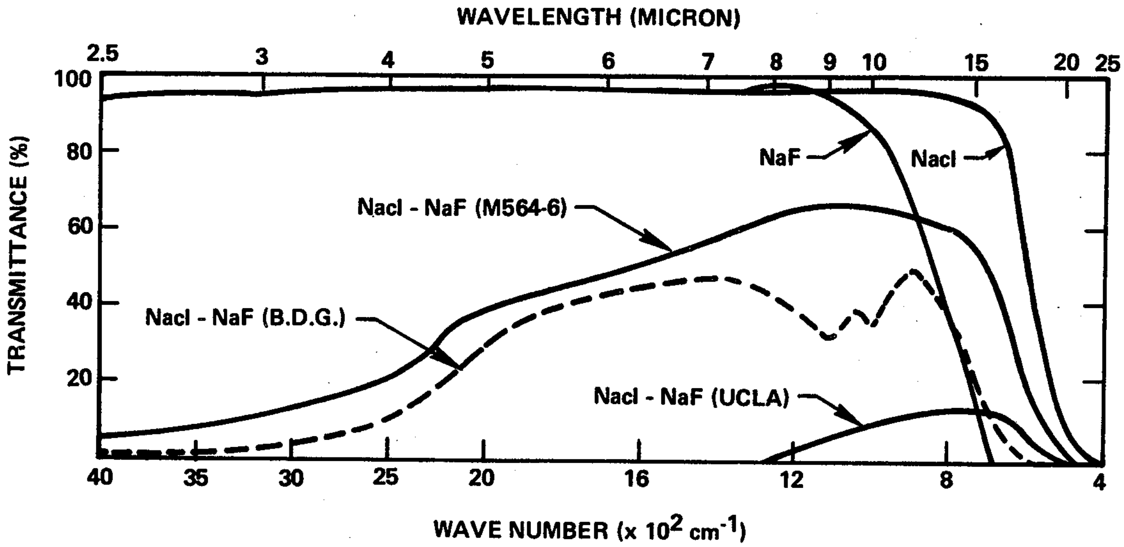



FIGURE 14. FAR-FIELD INFRARED TRANSMISSION CURVE FOR NaCl-NaF EUTECTICS GROWN ON EARTH AND IN SPACE. SAMPLE THICKNESS=0.107 in.

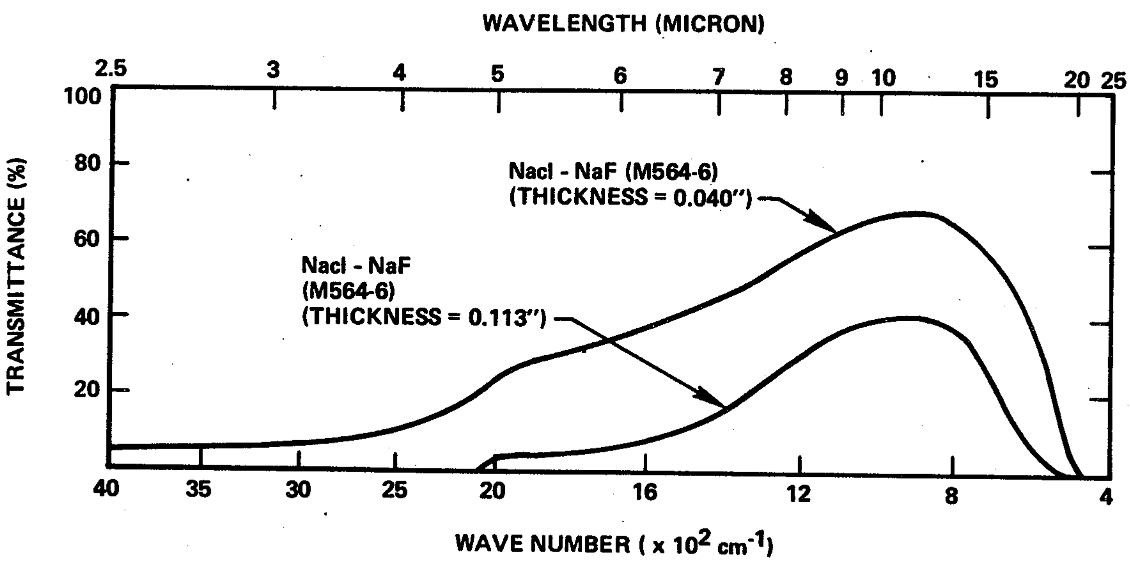



FIGURE 15. FAR-FIELD INFRARED TRANSMITTANCE CURVE FOR NaCl-NaF EUTECTICS OF DIFFERENT THICKNESS.

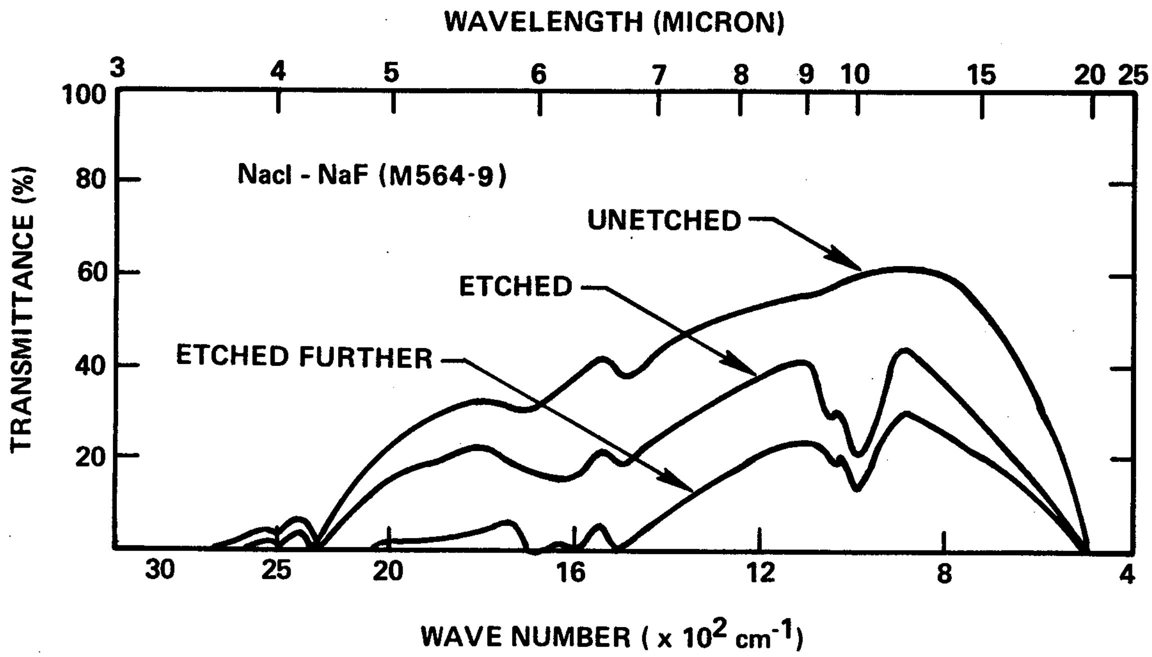



FIGURE 16. EFFECT OF SURFACE CONDITION ON FAR-FIELD INFRARED TRANSMITTANCE CURVE OF THE TRANSVERSE-SECTION SAMPLE. (THICKNESS = 0.035 ")

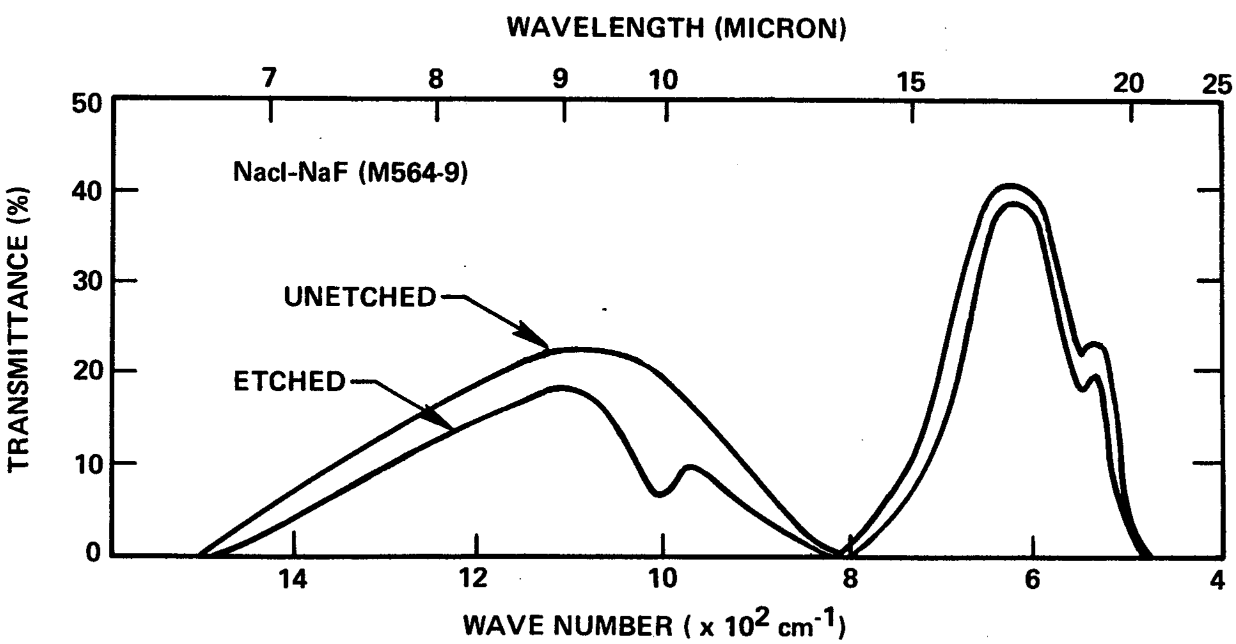



FIGURE 17. EFFECT OF SURFACE CONDITION ON FAR-FIELD INFRARED TRANSMITTANCE CURVE OF THE LONGITUDINAL-SECTION SAMPLE. (THICKNESS = 0.024")